

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the Production of a Catalyst for the Catalytic Hydration of Olefins into Alcohols

We, HIBERNIA-CHEMIE G.M.B.H., a Company incorporated under the laws of Germany, of Dortstenerstrasse 227, Gelsenkirchen-Buer, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of a catalyst for the catalytic hydration of olefins into alcohols.

It is known, that olefins in the gaseous phase may be converted into alcohols with steam under increased pressures. Processes of this nature are of especial technological importance in the production of ethyl alcohol from ethylene. The process is carried out in the presence of catalysts, the catalyst utilised as a rule being phosphoric acid deposited on carriers. The carriers which may be considered suitable for this purpose are, for example, activated charcoal, diatomaceous earth, and silicic acid. The carriers unfortunately as a rule possess the disadvantage of inadequate mechanical strength, so that the catalyst carrier must frequently be replaced, which represents a considerable cost as far as large-scale technological processes are concerned.

Other usable catalyst carriers are based on various forms of calcined diatomaceous earth. This carrier primarily consists of silicon dioxide in the form of complete or incomplete fossils of diatomaceae which are held or bonded together by means of clay or argillaceous substances. Although mechanical strength is substantially improved in carriers of this kind in comparison with silica gel, they possess the disadvantage that the iron and aluminium oxides contained therein are dissolved out during the reaction owing to the action of the phosphoric acid, which

leads to troublesome obstructions in equipment, particularly the regenerators. The catalyst carrier bakes into a solid mass after a relatively short operating period only, and must also be replaced by fresh catalyst carrier involving substantial expenditure each time.

In order to eliminate these drawbacks, it has already been proposed to subject catalyst carriers containing diatomaceous shells to a special treatment which consists of initially impregnating the carrier with phosphoric acid and subsequently treating it with steam at temperatures of up to 400°. A digestion process is subsequently carried out for an extended period with acidified water, and an impregnation with phosphoric acid is then repeated. The modified catalyst carriers so produced are characterised by increased resistance to wear as compared to the catalyst carriers known hitherto. They simultaneously exhibit satisfactory activity, and have proved satisfactory in productive application. Another advantage of these catalyst carriers is that obstructions are considerably reduced. A decrease in resistance to wear, however, also occurs in their case, after operating periods of a few months only. Accumulations of material worn away in powder form may thus clearly be observed in the lower part of the catalysis retort which cause substantial restriction of gas flow and thus allow of only limited operating periods.

The present invention is based on the surprising discovery, that catalyst carriers such as utilised for example in hydration and dehydration reactions, and in particular for the cleavage, isomerisation or reformation of hydrocarbon fractions, may after a certain treatment be utilised with excellent results as catalyst carriers for the catalytic hydration of olefins into alcohols. These catalyst carriers are of the type customary in the trade and produced in essentially

known manner starting with bentonite, and optionally using the addition of porcelain clay. Catalyst carriers of this kind contain a high proportion of montmorillonite-like minerals and in certain cases also beidellite, nontronite, hectorite, steatite and saucornite in addition to the montmorillonite. These known catalyst carriers contain varying amounts of aluminium and iron oxides.

The treatment followed as a rule in the production of such catalyst carriers is that the above-mentioned compounds are partially removed by treatment with an acid. It is also known to conduct the acid extraction such that practically all soluble compounds are removed from the starting material. In this last case, an aluminium compound must, however, be added again, since the catalyst carriers are not sufficiently active for "cleavage" reactions unless they have a minimum Al_2O_3 content. The catalyst carriers of the type specified and customary in the trade therefore as a rule possess an Al_2O_3 content of at least 15% by weight.

According to the present invention such aluminosilicate catalyst carriers produced in particulate form, for example of spheroid, cylinders, or lozenges, may be utilised with excellent results as catalyst carriers in the catalytic hydration of olefins into alcohols, provided they are treated with inorganic acids, aqueous HCl for example, at room temperature or at an elevated temperature up to the boiling point of the mixture, before proceeding with the catalyst acid impregnation, so as to reduce their Al_2O_3 content to below 10% by weight. The catalyst carriers produced in this manner surprisingly lose but little of their very high resistance against wear during this treatment, a high resistance being indispensable during the performance of cracking processes, e.g. in the gas stream. The mechanical strength of these catalyst carriers greatly exceeds that of the hydration catalysts known hitherto. These catalyst carriers also exhibit considerable absorptive capacity in respect of phosphoric acid.

In particular, the following procedure may be adopted in the production of these catalyst carriers. The catalyst carriers obtainable in the form of small spheroids of a diameter of 5 mms. are preferably digested with a 5% to 25% hydrochloric acid at an elevated temperature (e.g. 100°) until an Al_2O_3 content of 3% for example or less, is attained. The acid treatment may be continued until substantially the whole of the aluminium oxide which is soluble in phosphoric acid in the reaction conditions of the hydration (e.g. at 300°C) is removed. Surprisingly, it was found, that catalyst carriers of the type specified still possess adequate strength even when the treatment has been continued to reduce the Al_2O_3 content to

approximately 0.6% by weight. The amount of the aluminium oxide which is to be dissolved out in each particular instance naturally depends on the type of the preformed catalyst carrier substances treated. In general, it was found, that catalyst carriers which after the treatment according to the invention still possessed an Al_2O_3 content of between 5% and 1% by weight, possess excellent suitability for application in the catalytic hydration of olefins.

The acid treatment may be performed in one or more stages, where appropriate utilising different acid concentrations. The acid treatment may also be carried out in continuous manner. After the Al_2O_3 content required in each particular instance has been attained, the catalyst carrier is washed and dried, and may be digested again with steam and dried again. Sulphuric acid, and phosphoric acid, for example, may be utilised as acids in the treatment, instead of hydrochloric acid. Hydrochloric acid is preferred however, owing to its easier handling. An impregnation with phosphoric acid (preferably 50% to 85%) is carried out subsequently. The catalyst carrier may then be utilised immediately for the production of ethyl alcohol from ethylene and water.

As already stated, the catalyst carrier still possesses considerable strength after said treatment. The pore volume is also substantially increased at the same time. This is particularly surprising, since it was to be expected, that the acid treatment would lead to substantial alteration in the structure of the three-layer crystal lattice of the montmorillonite minerals owing to the substantial removal of the Al_2O_3 . In order to obtain a high pore volume it, therefore, proved advantageous to start with an initial material having as high as possible an Al_2O_3 content preferably exceeding 16%.

The high mechanical strength of the catalyst carrier produced according to the invention becomes apparent from the following comparison:

0.25 Kg. of a conventional cracking catalyst carrier in the form of spheroids made by the firm Suedchemie (trade name K 307), of up to 5 mms. in diameter, treated according to the present invention, was placed in a drum having a volumetric capacity of 5 litres. The drum is then made to rotate, and the amount of wear is measured after 100,000 revolutions. The wear amounts to 1.4% in the catalyst carrier treated according to the invention. For comparison, an identical quantity was utilised of a diatomaceous shell catalyst carrier in the form of cylindrical units (5×2 mms.), in the same conditions. This catalyst carrier had previously been subject to special processing, i.e. having first been impregnated with phosphoric acid, then treated with steam for 3

hours at 300°, subsequently being cooled and digested for an hour with acidified water at 100°, finally being washed free of acid and dried at 125°. An amount of wear of 10% resulted after 100,000 revolutions of the drum.

Apart from the substantially extended longevity of the catalyst carrier according to the invention as compared to the diatomaceous catalyst carrier, an additional advantage becomes apparent. Whereas approximately 1 Kg. of 100% phosphoric acid is required per 200 to 400 litres of alcohol produced in the case of the known catalyst carrier, it is possible to produce 1,000 to 4,000 litres of alcohol with the identical quantity, in the case of the catalyst carrier according to the invention. Relative to catalyst volume, one thus attains substantially higher outputs, which is presumably due to the increased pore volume. The catalyst carrier according to the invention is substantially cheaper moreover than the known catalyst carriers.

An acid treatment according to the present invention is not required, if it is possible to utilise catalyst carriers from the start, in which the aluminium oxide content soluble in acid in the reaction conditions of the hydration has already been substantially removed. A short subsequent acid treatment of such substances may in certain conditions also be adequate.

Instead of starting materials containing bentonite, one may also utilise as starting materials, preformed catalyst carriers of other inorganic alumino-silicates, such as kaolin for example, provided that the preformed carriers which are to be processed exhibit adequate mechanical strength. The alumina content of such preformed catalyst carriers is reduced to less than 10% before they are impregnated with phosphoric acid in accordance with the invention.

In order that the invention may be clearly understood a preferred embodiment in accordance therewith will now be described by way of example.

EXAMPLE

250 grams of a cracking catalyst carrier containing bentonite made by the firm

Suedchemie AG (trade name K 307) in the form of spheroids (diameter approx. 5 mms.) was treated with 400 cc. of a 20% hydrochloric acid at 100° to 110° C, and subsequently washed with 500 cc of water. After said treatment had been carried out for a total of five times, a drying operation by means of air was performed at approx. 110° to 120° C. The pore volume then amounted to 720 to 800 cc/Kg of carrier. Impregnation with 70% phosphoric acid was then performed until saturation was complete; the excess of phosphoric acid was allowed to drain off. This was followed by drying with air at 110°—120° C. The carrier had absorbed 450 grammes of phosphoric acid per Kg. of carrier.

If a catalyst carrier produced in this manner is utilised in the known conditions for the production of ethyl alcohol from ethylene and water, it is possible without difficulty to reach catalyst carrier operation periods substantially exceeding one year.

WHAT WE CLAIM IS:—

1. Process for the production of a catalyst for the catalytic hydration of olefins into alcohols, characterised by the fact, that a preformed catalyst carrier of inorganic alumino-silicates having an Al_2O_3 content of less than 10% by weight is impregnated with phosphoric acid.

2. Process according to Claim 1, wherein the catalyst carrier has an Al_2O_3 content of between 5% and 1% by weight.

3. The process for the production of a catalyst in accordance with Claim 1 substantially as herein before described.

4. The process for producing a catalyst substantially as hereinbefore described with reference to the Example.

5. Catalysts whenever prepared by the process of any one of Claims 1 to 4.

6. A process for catalytically hydrating olefins to form alcohols wherein the catalyst employed is one according to Claim 5.

7. Alcohols whenever produced by the process of Claim 6.

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